

Practitioner's Docket No. P-1118

10/049744
Express Mail No. ET998037948US

JC10 Rec'd PCT/PTO 30 JAN 2002

CHAPTER II

Preliminary Classification:

Proposed Class:

Subclass:

NOTE: "All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P., § 601, 7th ed.

**TRANSMITTAL LETTER
TO THE UNITED STATES ELECTED OFFICE (EO/US)
(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)**

PCT/ EP 00/06507	09 July 2000	30 July 1999
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
METHOD FOR PRODUCING A CATALYST BY ACID ACTIVATION		
TITLE OF INVENTION		
Uwe Flessner		
APPLICANT(S)		

Box PCT
Assistant Commissioner for Patents
Washington D.C. 20231
ATTENTION: EO/US

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is **mandatory**;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

- ☒ deposited with the United States Postal Service in an envelope addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231
37 C.F.R. § 1.8(a)
- ☐ with sufficient postage as first class mail.
- ☒ as "Express Mail Post Office to Addressee"
Mailing Label No. ET 998037948US (mandatory)
37 C.F.R. § 1.10 *

TRANSMISSION

- ☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: Jan 30, 2002

Signature

Dorothy Goodlett

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal Letter to the United States Elected Office (EO/US) [13-18]—page 1 of 9)

NOTE: To avoid abandonment of the application, the applicant shall furnish to the USPTO, not later than 20 months from the priority date: (1) a copy of the international application, unless it has been previously communicated by the International Bureau or unless it was originally filed in the USPTO; and (2) the basic national fee (see 37 C.F.R. § 1.492(a)). The 30-month time limit may not be extended. 37 C.F.R. § 1.495.

WARNING: Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail procedure of 37 C.F.R. § 1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing—See 37 C.F.R. § 1.8.

NOTE: Documents and fees must be clearly identified as a submission to enter the national state under 35 U.S.C. § 371 otherwise the submission will be considered as being made under 35 U.S.C. § 111. 37 C.F.R. § 1.494(f).

- I. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. § 371:
- a. ☒ This express request to immediately begin national examination procedures (35 U.S.C. § 371(f)).
 - b. ☒ The U.S. National Fee (35 U.S.C. § 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

2. Fees

CLAIMS FEE	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
<input checked="" type="checkbox"/> *	TOTAL CLAIMS				
	28	- 20 =	8	× \$18.00 =	\$ 144.00
	INDEPENDENT CLAIMS				
	4	- 3 =	1	\$84.00 × \$80.00 =	84.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$270.00					
BASIC FEE**	<input type="checkbox"/> U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an International preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO: <input type="checkbox"/> and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(1) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 C.F.R. § 1.492(a)(4)) \$100.00 <input type="checkbox"/> and the above requirements are not met (37 C.F.R. § 1.492(a)(1)) \$690.00				
	<input checked="" type="checkbox"/> U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO: <input type="checkbox"/> has been paid (37 C.F.R. § 1.492(a)(2)) \$710.00 <input type="checkbox"/> has not been paid (37 C.F.R. § 1.492(a)(3)) \$1000.00 <input checked="" type="checkbox"/> where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 C.F.R. § 1.492(a)(5)) \$860.00				860.00
	Total of above Calculations				= \$1088.00
	Reduction by 1/2 for filing by small entity, if applicable. Assertion must be made. (note 37 C.F.R. § 1.27)				-
	Subtotal				
SMALL ENTITY	Total National Fee				\$1088.00
	Fee for recording the enclosed assignment document \$40.00 (37 C.F.R. § 1.21(h)). (See Item 13 below). See attached "ASSIGNMENT COVER SHEET".				
	Total Fees enclosed				\$1088.00
TOTAL					\$1088.00

*See attached Preliminary Amendment Reducing the Number of Claims.

- ☒ Attached is a ☒ check ☐ money order in the amount of \$ 1,088.00
☒ Authorization is hereby made to charge the amount of \$
☒ to Deposit Account No. 03-3420
☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

WARNING: Credit card information should not be included on this form as it may become public.

- ☒ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

A duplicate of this paper is attached.

****WARNING:** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date: * * * (2) the basic national fee (see § 1.492(a)). The 30-month time limit may not be extended." 37 C.F.R. § 1.495(b).

WARNING: If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office. 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

☐ **Assertion of Small Entity Status**

☐ **Applicant hereby asserts status as a small entity under 37 C.F.R. § 1.27.**

NOTE: 37 C.F.R. § 1.27(c) deals with the assertion of small entity status, whether by a written specific declaration thereof or by payment as a small entity of the basic filing fee or the fee for the entry into the national phase as states:

"(c) Assertion of small entity status. Any party (person, small business concern or nonprofit organization) should make a determination, pursuant to paragraph (f) of this section, of entitlement to be accorded small entity status based on the definitions set forth in paragraph (a) of this section, and must, in order to establish small entity status for the purpose of paying small entity fees, actually make an assertion of entitlement to small entity status, in the manner set forth in paragraphs (c)(1) or (c)(3) of this section, in the application or patent in which such small entity fees are to be paid.

(1) Assertion by writing. Small entity status may be established by a written assertion of entitlement to small entity status. A written assertion must:

- (i) Be clearly identifiable;
- (ii) Be signed (see paragraph (c)(2) of this section); and
- (iii) Convey the concept of entitlement to small entity status, such as by stating that applicant is a small entity, or that small entity status is entitled to be asserted for the application or patent. While no specific words or wording are required to assert small entity status, the intent to assert small entity status must be clearly indicated in order to comply with the assertion requirement.

(2) Parties who can sign and file the written assertion. The written assertion can be signed by:

- (i) One of the parties identified in §§ 1.33(b) (e.g., an attorney or agent registered with the Office), §§ 3.73(b) of this chapter notwithstanding, who can also file the written assertion;
- (ii) At least one of the individuals identified as an inventor (even though a §§ 1.63 executed oath or declaration has not been submitted), notwithstanding §§ 1.33(b)(4), who can also file the written assertion pursuant to the exception under § 1.33(b) of this part; or
- (iii) An assignee of an undivided part interest, notwithstanding §§ 1.33(b)(3) and 3.73(b) of this chapter, but the partial assignee cannot file the assertion without resort to a party identified under §§ 1.33(b) of this part.

(3) Assertion by payment of the small entity basic filing or basic national fee. The payment, by any party, of the exact amount of one of the small entity basic filing fees set forth in §§ 1.16(a), (f), (g), (h), or (k), or one of the small entity basic national fees set forth in §§ 1.492(a)(1), (a)(2), (a)(3), (a)(4), or (a)(5), will be treated as a written assertion of entitlement to small entity status even if the type of basic filing or basic national fee is inadvertently selected in error.

(i) If the Office accords small entity status based on payment of a small entity basic filing or basic national fee under paragraph (c)(3) of this section that is not applicable to that application, any balance of the small entity fee that is applicable to that application will be due along with the appropriate surcharge set forth in §§ 1.16(e), or §§ 1.16(f).

(ii) The payment of any small entity fee other than those set forth in paragraph (c)(3) of this section (whether in the exact fee amount or not) will not be treated as a written assertion of entitlement to small entity status and will not be sufficient to establish small entity status in an application or a patent."

3. ☒ A copy of the International application as filed (35 U.S.C. § 371(c)(2)):

NOTE: Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment. "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☐ is transmitted herewith.
- b. ☐ is not required, as the application was filed with the United States Receiving Office.
- c. ☒ has been transmitted
 - i. ☒ by the International Bureau.

Date of mailing of the application (from form PCT/1B/308):

- ii. ☐ by applicant on _____. (Date)

4. ☒ A translation of the International application into the English language (35 U.S.C. § 371(c)(2)):

- a. ☒ is transmitted herewith.
- b. ☐ is not required as the application was filed in English.
- c. ☐ was previously transmitted by applicant on _____. (Date)
- d. ☐ will follow.

5. ☒ Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. § 371(c)(3)):

NOTE: The Notice of January 7, 1993 points out that 37 C.F.R. § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that: "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1.121. In many cases, filing an amendment under section 1.121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O.G. 29-40, at 36.

- a. ☐ are transmitted herewith.
- b. ☒ have been transmitted
 - i. ☐ by the International Bureau.
Date of mailing of the amendment (from form PCT/1B/308):

 - ii. ☒ by applicant on 12 Dec, 2001 (Date)
- c. ☐ have not been transmitted as
 - i. ☐ applicant chose not to make amendments under PCT Article 19.
Date of mailing of Search Report (from form PCT/ISA/210.):

 - ii. ☐ the time limit for the submission of amendments has not yet expired. The amendments or a statement that amendments have not been made will be transmitted before the expiration of the time limit under PCT Rule 46.1.

6. ☒ A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. § 371(c)(3)):
- a. ☒ is transmitted herewith.
 - b. ☐ is not required as the amendments were made in the English language.
 - c. ☐ has not been transmitted for reasons indicated at point 5(c) above.

7. ☒ A copy of the international examination report (PCT/IPEA/409)
- ☒ is transmitted herewith.
 - ☐ is not required as the application was filed with the United States Receiving Office.

8. ☐ Annex(es) to the international preliminary examination report
- a. ☐ is/are transmitted herewith.
 - b. ☐ is/are not required as the application was filed with the United States Receiving Office.

9. ☐ A translation of the annexes to the international preliminary examination report
- a. ☐ is transmitted herewith.
 - b. ☐ is not required as the annexes are in the English language.

10. ☒ An oath or declaration of the inventor (35 U.S.C. § 371(c)(4)) complying with 35 U.S.C. § 115
- a. ☐ was previously submitted by applicant on _____. (Date)
 - b. ☐ is submitted herewith, and such oath or declaration
 - i. ☐ is attached to the application.
 - ii. ☐ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. § 1.70.
 - c. ☒ will follow.

II. Other document(s) or information included:

11. ☒ An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a):
- a. ☒ is transmitted herewith.
 - b. ☐ has been transmitted by the International Bureau.
Date of mailing (from form PCT/IB/308): _____.
 - c. ☐ is not required, as the application was searched by the United States International Searching Authority.
 - d. ☐ will be transmitted promptly upon request.
 - e. ☐ has been submitted by applicant on _____. (Date)
12. ☒ An Information Disclosure Statement under 37 C.F.R. §§ 1.97 and 1.98:
- a. ☐ is transmitted herewith.

Also transmitted herewith is/are:

- ☐ Form PTO-1449 (PTO/SB/08A and 08B).
 - ☐ Copies of citations listed.
 - b. ☒ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. § 371(c).
 - c. ☐ was previously submitted by applicant on _____. (Date)
13. ☐ An assignment document is transmitted herewith for recording.
A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

14. ☒ Additional documents:
- a. ☐ Copy of request (PCT/RO/101)
 - b. ☐ International Publication No. _____
 - i. ☐ Specification, claims and drawing
 - ii. ☐ Front page only
 - c. ☒ Preliminary amendment (37 C.F.R. § 1.121)
 - d. ☐ Other

15. ☒ The above checked items are being transmitted
- a. ☒ before 30 months from any claimed priority date.
 - b. ☐ after 30 months.

16. ☐ Certain requirements under 35 U.S.C. § 371 were previously submitted by the applicant on _____, namely:

AUTHORIZATION TO CHARGE ADDITIONAL FEES

WARNING: Accurately count claims, especially multiple dependant claims, to avoid unexpected high charges if extra claims are authorized.

NOTE: "A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).

NOTE: "Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).

- ☒ Please charge, in the manner authorized above, the following additional fees that may be required by this paper and during the entire pendency of this application:
- ☒ 37 C.F.R. § 1.492(a)(1), (2), (3), and (4) (filing fees)

WARNING: Because failure to pay the national fee within 30 months without extension (37 C.F.R. § 1.495(b)(2)) results in abandonment of the application, it would be best to always check the above box.

(Transmittal Letter to the United States Elected Office (EO/US) [13-18]—page 8 of 9)

☒ 37 C.F.R. § 1.492(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.

☐ 37 C.F.R. § 1.17 (application processing fees)

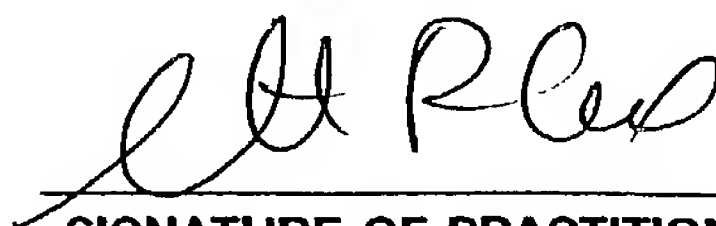
☐ 37 C.F.R. § 1.17(a)(1)-(5) (extension fees pursuant to § 1.136(a).

☐ 37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. § 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying . . . issue fee." From the wording of 37 C.F.R. § 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

☐ 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).



SIGNATURE OF PRACTITIONER

Scott R. Cox

(type or print name of practitioner)

400 West Market St., Suite 2200

P.O. Address

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Customer No.:

JC13 Rec'd PCT/PTO 30 JAN 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of
Uwe Flessner

Serial No.

Filing Date

Attorney Docket No. P-1118

For: METHOD FOR PRODUCING A
CATALYST BY ACID ACTIVATION:
:
:
:
:
:
:
:
:
:

Art Unit:

Examiner:

*Sub Spec*Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Attention: EO/US

PRELIMINARY AMENDMENT

The attached application is a translation of PCT application, PCT/EP 00/06507, WO 01/08796 A1. The application was originally filed in Germany on July 30, 1999 as application DE 199 35 914.8. A copy of the translation with handwritten amendments to that application is attached as Exhibit A. Attached as Exhibit B is the application with those handwritten amendments incorporated therein along with new Claims 1-28. Please cancel all prior claims.

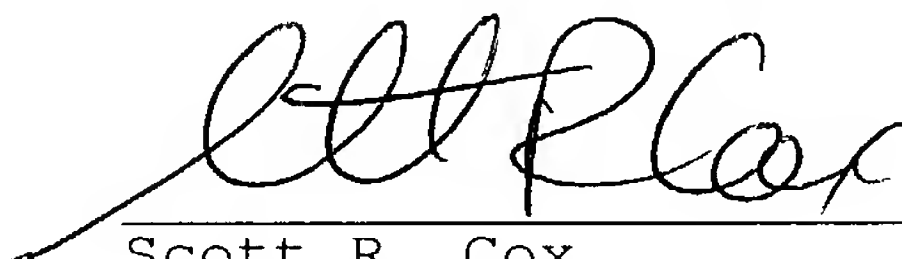
The translation of the application contained a number of minor translation errors and awkward wording. The applicant has made minor amendments to the application to correct these errors as shown in the handwritten modifications to the application in Exhibit A. These amendments are incorporated into the application

which is contained in Exhibit B. No new subject matter is introduced by any of these amendments. Rather, the application is merely placed in better condition for review by the United States Patent and Trademark Office.

CONCLUSION

The applicant requests that the amendments be accepted and the application along with new Claims 1-28 which are contained in Exhibit B be reviewed by the United States Patent and Trademark Office.

Respectfully submitted,



Scott R. Cox
Reg. No. 31,945
LYNCH, COX, GILMAN & MAHAN, P.S.C.
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Louisville, Kentucky 40202
(502) 589-4215

Attachments

CERTIFICATE OF SERVICE

I hereby certify that this correspondence is being deposited with the United States Postal Service in an envelope as Express Mail Post Office to Addressee," mailing Label Number ET998037948US, addressed to Box PCT, Attn: EO/US, Assistant Commissioner for Patents, Washington, D.C. 20231.

Dated:

Jan 30, 2002

Dorothy Goodlett

SRC:dg
C:\WP\PAT\P1118.PAM
1-30-02
411180

JC18 Rec'd PCT/PTO 30 JAN 2002

~~TRANSLATION FROM GERMAN~~

Title
~~Patent Application~~

Process for producing catalysts by acid activation

Specification

to
The invention relates a process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions.

Catalysts based on phyllosilicates, for example, clays, are used in many technical reactions. But naturally occurring clays, such as for example montmorillonite, kaolin, or attapulgite, in part have overly low activities. For this reason the clays for producing catalysts are often activated by treatment with acid. On the one hand, pure ~~coating~~ with for example sulfuric acid and, on the other hand, activation by extraction of the raw clay with acid, generally sulfuric or hydrochloric acid, can be done.

covering
Thus, according to US-A-3,452,056 an acid-~~coated~~ *covered* montmorillonite catalyst (KSF/0) is used for alkylation of diphenylamine. According US-A-5,672,752 an acid-extracted montmorillonite is used for the same reaction. Catalysts of this type are available under the commercial name Retrol^x, Fulcat^x and K10. According to US-A-5,043,511, as a replacement for corrosive homogeneous catalysts, for example $AlCl_3$ or BCl_3 , heterogeneous catalysts are used which are produced by coextrusion of clays with two different metal salts and thermal treatment at temperatures from 300°C to 800°C. Products produced in this way

are used as catalysts for alkylation of, for example, benzene with olefins.

But these modified clays also have disadvantages, for example, rapid deactivation or a complex production process, and there have been many efforts to eliminate these defects. Thus, US-A-2,464,127 reports on a two-stage process with the object of obtaining amounts of iron as small as possible in the end product of acid activation of montmorillonite. According US-A-2,574,895, some of ^{the} salts extracted in acid treatment are precipitated again on the montmorillonite-containing material, reducing reagents which are intended to prevent the iron from settling in the precipitation process ~~however~~ being used. The effort to increase the service life of the resulting catalysts by reduced coke formation is common to both applications.

DE-A-1 271 682 describes a process for activation of montmorillonite^s by acid extraction in the presence of inert organic liquid compounds. Strong acids, such as for example hydrochloric or sulfuric acid, are used for acid activation. Due to the presence of organic components during decomposition of the clay by acid, the lattice distances of the resulting montmorillonite catalyst are increased, by which more catalyst centers become accessible to the substrate. The catalysts according DE-A-1 271 682 are used for alkylation of phenolic compounds.

Other methods of activation are described in EP-A-352 878. In this case an untreated clay is ^{covered} ~~coated~~ by impregnation with, for example, zinc salts, copper salts or nickel salts. Organic solvents of the metal salts are used, ^{the} solvent is removed by distillation after impregnation. According to EP-A-144 219 and EP-A-031 252 raw clays are activated by a similar impregnation technique or by ion exchange. In ion exchange the natural intercalate cations of the minerals, mainly sodium, calcium and magnesium, are replaced by catalytically active metals. ~~But~~ ^{The}

To overcome this disadvantage, Laszlo in Helvetica Chimica Acta 70 (1987) 577 describes subsequent metal ion activation of already acid-activated montmorillonites. Thus, the commercially available catalyst K10 which is rich in pores and which is produced by acid activation of bentonite is modified by ion exchange with various metal salts. To do this the K10 present as a powder in a methanolic slurry is treated with solutions of the metal salts for several hours. The amount of metal ions used is computed such that they are present in a roughly 30- to 40-fold excess relative to the ion exchange capacity of the K10. Then the mixture is separated by filtration and the catalyst is washed free of salt^s and then dried. Especially good effects are achieved by ion exchange with aluminum salts and titanium salts. Replacement with iron salts leads to improved reactivity of the catalyst only in a few cases.

A similar process is also used by Cativiela in Appl. Cat. A 123 (1995) 273. Cativiela calcinates the catalysts additionally at temperatures around 500°C in order to reduce the Brönsted activity. In this publication good activities are achieved especially with cerium salts. Replacement with iron ions however does not show any special effects.

The process used in these activation methods has at least two disadvantages. On the one hand, the process consists of two component processes which are independent of one another, specifically the acid activation of raw clays and the subsequent ion exchange reaction. Secondly, the ion exchange reaction must be carried out at a high ion excess. This necessarily leads to

EP-B 284 397 describes a process in which the clay to be activated by the ion exchange is replaced in an upstream step with lithium ions and then thermally treated. With the resulting intermediate product ion exchange is then carried out in a second process step. Metal ions which are preferably used for this purpose are aluminum ions. Li clays with replaced iron ions do not show any improved activity compared to the initial material.

The object of this invention was to produce catalysts which have been modified with metal ions, and simple process steps and small waste water flows were to be guaranteed.

The subject matter of the invention is thus a process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions, ~~it is~~ characterized in that the acid activation is carried out in the presence of catalytically active metal ions, ~~and~~ ^T the solution which is formed during acid activation together with the residual solution which contains the excess, catalytically active cations ^{then} ~~is~~ separated.

~~Preferred embodiments of the process as claimed in the~~
~~invention are given in the dependent claims.~~

It has been surprisingly found that highly active catalysts can be obtained ~~in~~ the acid activation of phyllosilicates in the presence of activating ions. In doing so it is not necessary to carry out activation and ion exchange in separate process steps. In the process as claimed in the invention, ~~completely~~ unexpectedly small amounts of the catalytically active ions are

^{necessary} ~~sufficient~~, ^{T process} this ~~can~~ reduce^s process costs, ^{and reduces} ~~but also~~ the environmental burden of the process to a minimum. In certain cases, as for example ^{with} in activation with iron ions or aluminum ions, the spent liquors obtained ~~in this way~~ can even be used as precipitation aids in the clean-up of municipal sewage. It has furthermore been ascertained that the metal ions used for modification are present in an especially high degree of activation so that the amount of metal ions present in the final product can be kept especially low.

The subject matter of the invention is also the use of catalysts ~~which can be~~ obtained using the process as claimed in the invention for proton-catalyzed reactions, especially for conversion of higher olefins with aromatic hydroxy compounds and amines, for esterification and dehydration reactions as well as for purification of xylene and for Lewis acid-catalyzed reactions, such as for example alkylation of aromatics.

^{illustrated}
The invention is ~~explained~~ by the following examples.

Example 1

Comparison catalyst

A previously dried Bavarian montmorillonite-containing raw clay with an ion exchange capacity (~~HUF~~) of 80 mVal/100 g was decomposed by hydrochloric acid treatment.

To determine the ^{ION} ~~acid~~ exchange capacity (~~HUF~~), the phyllosilicate to be studied ^{was} ~~is~~ dried over an time interval of 2 hours at 150°C. Then the dried material ^{was} ~~is~~ reacted with an excess of aqueous 2N NH₄Cl solution for one hour with reflux. After a holding time of 16 hours at room temperature it ^{was} ~~is~~ filtered, whereupon the filter cake ^{was} ~~is~~ washed, dried and ground and the NH₄ content in the phyllosilicate ^{was} ~~is~~ determined by

nitrogen determination (CHN analyzer from Leco). The proportion and type of exchanged metal ions ^{was} ~~are~~ determined in the filtrate by ICP spectroscopy.

During decomposition, 90.3 g of raw clay with a water content of 16.9% by weight together with 250.7 g water and 87.5 mg of 30% hydrochloric acid were treated in a three-neck flask with a reflux condenser for 8 hours at ~~the~~ boiling point. Afterwards the mother liquor was separated from the product by filtration by means of a Buchner funnel and washed using demineralized water until chloride could no longer be detected in the wash water. The washed filter cake was dried at a temperature of 120°C and then ground.

The product obtained in this way has a BET surface_A of 253 m²/g (according to DIN 66131) and a pore volume of 0.403 ml/g (determined by nitrogen adsorption and evaluation of the adsorption isotherms using the BJH method - E.P. Barret et al., J.Am.Chem.Soc. 73 (1951) 373). The pore distribution curve obtained from BJH derivation showed a Gaussian distribution with a maximum at 5.5 nm. The material contained among others the following exchangeable metal ions:

Fe ³⁺	1.0 mVal/100 g
Al ³⁺	11.4 mVal/100 g
Ce ³⁺	< 0.1 mVal/100 g

Example 2

Iron-containing catalyst

A Bavarian montmorillonite-containing raw clay with an ion exchange capacity ~~of~~ of 92 mVal/100 g was activated analogously to Example 1. In addition to the reagents indicated in Example 1, iron chloride in the form of a concentrated FeCl₃ solution was

added to the batch. The following were used for this batch:

Raw clay (17.2 % by weight H ₂ O)	82.8 g
Water	250.3 g
HCl (30%)	50.0 g
FeCl ₃ solution (2.5 mole Fe/kg)	6.0 g

area

The product obtained in this way had a BET surface_λ of 290 m²/g and a pore volume of 0.338 ml/g. The peak of the pore distribution curve was at 4.6 nm. The amount of exchangeable Fe³⁺ ions was 2.0 mVal/100 g.

Example 3

Iron-containing catalyst

Example 2 was repeated using 18.0 g FeCl₃ solution:

area

The product obtained in this way had a BET surface_λ of 400 m²/g and a BJH pore volume of 0.491 ml/g. The peak of the pore distribution curve was at 4.7 nm. The amount of exchangeable Fe³⁺ ions was 8.0 mVal/100 g.

Example 4

Aluminum-containing catalyst

Example 2 was repeated using 7.24 g AlCl₃ * 6 H₂O.

area

The product obtained in this way had a BET surface_λ of 315 m²/g and a BJH pore volume of 0.425 ml/g. The peak of the pore distribution curve was at 3.3 nm. The product contained 18.0 mVal/100 g exchangeable Al³⁺.

Example 5

Cerium-containing catalyst

A montmorillonite-containing raw clay from Turkey was dried to a water content of roughly 15% by weight and was ground. The material with a resulting water content of 13.1% by weight was activated as described in Example 1, the reaction mixture having been enriched with $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$. The following were used for this batch:

Raw clay (13.1 % by weight H_2O)	86.3 g
Water	254.6 g
HCl (30% by weight)	62.5 g
$\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$	13.03 g

Analysis of the product yielded a BET surface ^{area} of 379 m^2/g and a BJH pore volume of 0.431 ml/g. The peak of the pore distribution curve was at 3.0 nm. The product contained 5.1 mVal/100 g exchangeable Ce^{3+} .

Example 6

Reaction of phenol with nonene

The alkylation ^{reaction} example 11 ^{from} DE-A-1 271 682 was ^{reworked} analogously. In a 1 liter three-neck flask equipped with a thermometer, a magnetic stirring mechanism and a reflux condenser, 252.5 g (2.0 mole) nonene, 235.3 g (2.5 mole) phenol and 5.0 g catalyst from Example 2 and Example 3 were heated to 90°C. After 3 hours reaction time, the catalyst was filtered off. The filtrate was fractionated using a 10 cm Vigreux column. In the boiling range from 159°C to 181°C the alkylation product nonyl phenol was obtained.

As Table I shows, higher yields ^{were} ~~are~~ achieved with the catalysts as claimed in the invention compared to the undoped

catalyst (Example 1). The narrower boiling range for Fe-modified catalysts indicates a more uniform product spectrum and thus higher selectivity of the Fe-containing catalysts.

Table I

Alkylation of Phenol with Nonene

Catalyst	Boiling range of product	Yield
Example 1	160 - 180°C	35.3%
Example 2	165 - 175°C	38.7%
Example 3	173 - 175°C	41.2%

Example 7

Reaction of diphenylamine with nonene

In a 500 ml three-neck flask, 42.5 g (0.25 mole) diphenylamine were heated to roughly 150°C and melted. Then 5.0 g catalyst and 44.2 g (0.35 mole) nonene were added to the melt. After a reaction time of 4 h, a further 41.6 g (0.33 mole) nonene were added, the reaction temperature of 150°C having been maintained. After a reaction time of 8 h the reaction mixture was separated from the catalyst by filtration. The yield of dialkylated diphenylamine was determined by infrared spectroscopy using the following formula:

$$(\%) \text{ dialkylate} = [\text{Log}(\text{ext@ } 820 \text{ cm}^{-1} / \text{ext@ } 743 \text{ cm}^{-1}) + 1.141] / 0.019;$$

ext@ extinction (absorbance) at the indicated wave number. In doing so it was considered that the adsorption peak at 820 cm⁻¹ corresponds to the dialkylated products, ^{and} the adsorption peak at 743 cm⁻¹ corresponds to the monoalkylated products. The reaction mixture was measured at a layer thickness of 0.025 mm to determine extinction.

reaction time.

Table III

Esterification of Ethanol and Acetic Acid

	Conversion after 30 min (%)	Conversion after 60 min (%)
Example 1	10	13%
Example 2	20	28
Example 4	27	34

Example 9

Dehydration of Cyclohexanol

In a three-neck flask with an attached Vigreux column and distillation bridge, 250 ml cyclohexanol together with 5 g powdered catalyst as described in Example 3 and Example 5 were caused to boil. The products, cyclohexene and water, which formed during the reaction were continuously removed from the reaction space via the distillation bridge. The condensed amounts of water and cyclohexene were recorded as a function of the reaction time. After roughly 200 ml cyclohexanol were reacted, 250 ml substrate was again added to the reaction vessel. This process was repeated three times without a significant decrease of the reaction ^{rate}~~speed~~ being observed. The product formation rate for the catalyst according to Example 3 was 1.9 ml/min, for the catalyst according to Example 5 it was 1.7 ml/min.

The example confirms the ^{consistently}~~constant~~ high reactivity of the catalysts for proton-catalyzed reactions.

Example 10

Continuous Purification of Xylene

Some of the filter cake obtained after washing the product according to Example 5 was dried at 110°C and carefully crushed. The 0.25 mm to 0.50 mm grain fraction was screened out of the fragments. Five milliliters of these fractional granulates was placed in a 10 ml tube reactor through which industrial xylene flowed continuously via a HPLC pump. The tube reactor was heated by a temperature-controlled oil bath to 175°C, this temperature being kept constant during the experiment. To prevent gas bubble formation at this temperature, a back pressure regulator which regulated the working pressure in the reactor constantly to 30 bar was installed between the reactor and the likewise installed sampling valves. A LHSV (liquid hourly space velocity) value of 12h^{-1} was set via the HPLC pump.

The industrial xylene used has a bromine index of 580 mg/100 g due to the unsaturated aliphatic compounds. These unsaturated compounds were reacted on the granulated catalyst presumably by a Lewis acid-catalyzed alkylation reaction such that after treatment of the raw material the bromine index dropped to values less than 2 mg/100 g. Over time, deactivation of the catalyst which allowed the bromine index of the treated xylene to rise again took place. After reaching a bromine index of 20 mg/100 g, exhaustion of the catalyst was defined. The amount of xylene converted during this running time is a direct measure of the catalyst activity. Using the granulated catalyst as shown in Example 5, a running time of 18 days was achieved, a total of 25.86 l xylene having been converted. In a comparison test with a commercially available catalyst, the Süd-Chemie product Tonsil® CO 630 G, a total running time of 12 days with a xylene throughput of 17.24 liters was achieved during this time.

The example confirms the clear improvement of catalyst activity compared to the prior art.

Claims

1. ^A Process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions, characterized in that acid activation is carried out in the presence of catalytically active metal ions and the solution which forms during acid activation together with the remaining solution which contains the excess, catalytically active cations

one is separated.

^{The} 2. Process as claimed in claim 1, wherein acid activation is carried out in the presence of iron ions, aluminum ions, and/or cerium ions. *(this comprises)*

3. Process as claimed in claim 1 or 2, wherein phyllosilicates ^{the} *is selective from + the group contains of* from the group of smectites, chlorites, illites, vermiculites of the serpentine-kaolin group, and of the sepiolite-palygorskite group, especially montmorillonite, beidellite and nontronite, ^{the} are used.

^{The} 4. Process as claimed in one of claims 1 to 3, wherein acid activation is carried out in the presence of a waste liquor from earlier acid activation, which liquor contains aluminum ions and/or iron ions. ^{+ the} *comprise*

5. Process as claimed in one of claims 1 to 4, wherein the acid-activated phyllosilicates which are coated with the catalytically active metal ions are washed, dried and calcinated.

6. Use of catalysts which can be obtained using the process as claimed in one of claims 1 to 5 for proton-catalyzed or Lewis acid-catalyzed reactions, especially for conversion of higher olefins with aromatic hydroxy compounds and amines, for esterification and dehydration reactions and for purification of aromatics.

Abstract

A process for producing catalysts by acid activation of phyllosilicates and coating with catalytically active metal ions ~~is described~~ ^{whereby} acid activation is carried out in the presence of catalytically active metal ions, ~~and~~ ^{the} solution which forms during acid activation together with the remaining solution which contains the excess, catalytically active cations ~~is~~ ^{are} separated. The catalysts can be used for proton-catalyzed and Lewis acid-catalyzed reactions, especially for conversion of higher olefins with aromatic hydroxy compounds and amines, for esterification and dehydration reactions and for purification of aromatics.

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Süd-Chemie AG

Claims¹

1. Process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions, characterized in that acid activation is carried out in the presence of catalytically active [iron ions,] aluminum ions, and/or cerium ions and the solution which forms during acid activation together with the remaining solution which contains the excess, catalytically active cations is separated. [, the content of exchangeable iron ions being less than 2.5% by weight and more than 0.027% by weight, computed as Fe_2O_3].

2. Process as claimed in claim 1, wherein phyllosilicates from the group of smectites, chlorites, illites, vermiculites of the serpentine-kaolin group, and of the sepiolite-palygorskite group, especially montmorillonite, beidellite and nontronite, are used.

3. Process as claimed in claim 1 or 2, wherein acid activation is carried out in the presence of liquor from an earlier acid activation, which liquor contains aluminum ions [and/or iron ions].

¹ [Translator's note: Bracketed material below was marked as deleted in original German]

4. Process as claimed in one of claims 1 to 3, wherein the acid-activated phyllosilicates coated with the catalytically active metal ions are washed, dried and calcinated.

5. Use of catalysts which can be obtained using the process as claimed in one of claims 1 to 4 for proton-catalyzed or Lewis acid-catalyzed reactions, especially for conversion of higher olefins with aromatic hydroxy compounds and amines, for esterification and dehydration reactions and for purification of aromatics.

Title

5 Process for producing catalysts by acid activation

Specification

10 The invention relates to a process for producing catalysts
by acid activation of phyllosilicates and modification with
catalytically active metal ions.

15 Catalysts based on phyllosilicates, for example, clays,
are used in many technical reactions. But naturally occurring
clays, such as for example montmorillonite, kaolin, or
attapulgite, in part have overly low activities. For this
reason the clays for producing catalysts are often activated by
treatment with acid. On the one hand, pure covering with for
example sulfuric acid and, on the other hand, activation by
20 extraction of the raw clay with acid, generally sulfuric or
hydrochloric acid, can be done.

25 Thus, according to US-A-3,452,056 an acid-covered
montmorillonite catalyst (KSF/0) is used for alkylation of
diphenylamine. According US-A-5,672,752 an acid-extracted
montmorillonite is used for the same reaction. Catalysts of
this type are available under the commercial name Retrol,
Fulcat and K10. According to US-A-5,043,511, as a replacement
for corrosive homogeneous catalysts, for example AlCl_3 or BCl_3 ,
30 heterogeneous catalysts are used which are produced by
coextrusion of clays with two different metal salts and thermal
treatment at temperatures from 300°C to 800°C . Products
produced in this way are used as catalysts for alkylation of,
for example, benzene with olefins.

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natural intercalate cations of the minerals, mainly sodium, calcium and magnesium, are replaced by catalytically active metals. The disadvantage in this process is that the catalysts produced have an overly low pore volume. This means that only the outer surface is accessible to the substrates. Most of the inner surfaces of the catalysts are, however, not accessible. Thus, a large part of the possible activity remains unused.

To overcome this disadvantage, Laszlo in Helvetica Chimica Acta 70 (1987) 577 describes subsequent metal ion activation of already acid-activated montmorillonites. Thus, the commercially available catalyst K10 which is rich in pores and which is produced by acid activation of bentonite is modified by ion exchange with various metal salts. To do this the K10 present as a powder in a methanolic slurry is treated with solutions of the metal salts for several hours. The amount of metal ions used is computed such that they are present in a roughly 30- to 40-fold excess relative to the ion exchange capacity of the K10. Then the mixture is separated by filtration and the catalyst is washed free of salts and then dried. Especially good effects are achieved by ion exchange with aluminum salts and titanium salts. Replacement with iron salts leads to improved reactivity of the catalyst only in a few cases.

A similar process is also used by Cativiela in Appl. Cat. A 123 (1995) 273. Cativiela calcinates the catalysts additionally at temperatures around 500°C in order to reduce the Brönsted activity. In this publication good activities are achieved especially with cerium salts. Replacement with iron ions however does not show any special effects.

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It has been surprisingly found that highly active catalysts can be obtained from the acid activation of phyllosilicates in the presence of activating ions. In doing so it is not necessary to carry out activation and ion exchange in separate process steps. In the process as claimed in the invention, unexpectedly small amounts of the catalytically active ions are necessary. This process reduces process costs, and reduces the environmental burden of the process to a minimum. In certain cases, as for example with activation with iron ions or aluminum ions, the spent liquors obtained can even be used as precipitation aids in the clean-up of municipal sewage. It has furthermore been ascertained that the metal ions used for modification are present in an especially high degree of activation so that the amount of metal ions present in the final product can be kept especially low.

The invention is illustrated by the following examples.

Comparison catalyst

A previously dried Bavarian montmorillonite-containing raw

clay with an ion exchange capacity (IEC) of 80 mVal/100 g was decomposed by hydrochloric acid treatment.

To determine the ion exchange capacity (IEC), the phyllosilicate to be studied was dried over an time interval of 2 hours at 150°C. Then the dried material was reacted with an excess of aqueous 2N NH_4Cl solution for one hour with reflux. After a holding time of 16 hours at room temperature it was filtered, whereupon the filter cake was washed, dried and ground and the NH_4 content in the phyllosilicate was determined by nitrogen determination (CHN analyzer from Leco). The proportion and type of exchanged metal ions was determined in the filtrate by ICP spectroscopy.

During decomposition, 90.3 g of raw clay with a water content of 16.9% by weight together with 250.7 g water and 87.5 mg of 30% hydrochloric acid were treated in a three-neck flask with a reflux condenser for 8 hours at boiling. Afterwards the mother liquor was separated from the product by filtration by means of a Buchner funnel and washed using demineralized water until chloride could no longer be detected in the wash water. The washed filter cake was dried at a temperature of 120°C and then ground.

The product obtained in this way has a BET surface area of 253 m^2/g (according to DIN 66131) and a pore volume of 0.403 ml/g (determined by nitrogen adsorption and evaluation of the adsorption isotherms using the BJH method - E.P. Barret et al., J.Am.Chem.Soc. 73 (1951) 373). The pore distribution curve obtained from BJH derivation showed a Gaussian distribution with a maximum at 5.5 nm. The material contained among others the following exchangeable metal ions:

Fe ³⁺	1.0 mVal/100 g
Al ³⁺	11.4 mVal/100 g
Ce ³⁺	< 0.1 mVal/100 g

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Example 2Iron-containing catalyst

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A Bavarian montmorillonite-containing raw clay with an ion exchange capacity IEC of 92 mVal/100 g was activated analogously to Example 1. In addition to the reagents indicated in Example 1, iron chloride in the form of a concentrated FeCl₃ solution was added to the batch. The following were used for this batch:

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Raw clay (17.2 % by weight H ₂ O)	82.8 g
Water	250.3 g
HCl (30%)	50.0 g
FeCl ₃ solution (2.5 mole Fe/kg)	6.0 g

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The product obtained in this way had a BET surface area of 290 m²/g and a pore volume of 0.338 ml/g. The peak of the pore distribution curve was at 4.6 nm. The amount of exchangeable Fe³⁺ ions was 2.0 mVal/100 g.

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Example 3Iron-containing catalyst

Example 2 was repeated using 18.0 g FeCl₃ solution:

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The product obtained in this way had a BET surface area of 400 m²/g and a BJH pore volume of 0.491 ml/g. The peak of the pore distribution curve was at 4.7 nm. The amount of

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exchangeable Fe^{3+} ions was 8.0 mVal/100 g.

Example 4

Aluminum-containing catalyst

5 Example 2 was repeated using 7.24 g $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$.

10 The product obtained in this way had a BET surface area of 315 m^2/g and a BJH pore volume of 0.425 ml/g. The peak of the pore distribution curve was at 3.3 nm. The product contained 18.0 mVal/100 g exchangeable Al^{3+} .

Example 5

Cerium-containing catalyst

15 A montmorillonite-containing raw clay from Turkey was dried to a water content of roughly 15% by weight and was ground. The material with a resulting water content of 13.1% by weight was activated as described in Example 1, the reaction
20 mixture having been enriched with $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$. The following were used for this batch:

	Raw clay (13.1 % by weight H_2O)	86.3 g
	Water	254.6 g
25	HCl (30% by weight)	62.5 g
	$\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$	13.03 g

30 Analysis of the product yielded a BET surface area of 379 m^2/g and a BJH pore volume of 0.431 ml/g. The peak of the pore distribution curve was at 3.0 nm. The product contained 5.1 mVal/100 g exchangeable Ce^{3+} .

Reaction of phenol with nonene

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Alkylation of Phenol with Nonene

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In a 500 ml three-neck flask, 42.5 g (0.25 mole)

diphenylamine were heated to roughly 150°C and melted. Then 5.0 g catalyst and 44.2 g (0.35 mole) nonene were added to the melt. After a reaction time of 4 h, a further 41.6 g (0.33 mole) nonene were added, the reaction temperature of 150°C having been maintained. After a reaction time of 8 h the reaction mixture was separated from the catalyst by filtration. The yield of dialkylated diphenylamine was determined by infrared spectroscopy using the following formula:

$$(\%) \text{ dialkylate} = [\text{Log}(\text{ext@ } 820 \text{ cm}^{-1} / \text{ext@ } 743 \text{ cm}^{-1}) + 1.141] / 0.019;$$

ext@ extinction (absorbance) at the indicated wave number. In doing so it was considered that the adsorption peak at 820 cm⁻¹ corresponds to the dialkylated products, and the adsorption peak at 743 cm⁻¹ corresponds to the monoalkylated products. The reaction mixture was measured at a layer thickness of 0.025 mm to determine extinction.

Table II lists the determined yields of the reaction with various catalysts.

Table II
Alkylation of Diphenylamine with Nonene

Catalyst	Yield of dinonyl-diphenylamine (%)
Example 1	27
Example 3	40
Example 4	37
Example 5	35

The example confirms the improved activity of the catalysts as claimed in the invention in diphenylamine

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alkylation compared to the prior art.

Example 8

Esterification of acetic acid and ethanol

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In a 250 ml three-neck flask with a thermometer, a magnetic stirring mechanism and a reflux condenser, 72.0 g acetic acid and 55.2 g ethanol were mixed. Roughly 0.5 g was removed from the mixture, and the acid content was determined by titration with 0.1N sodium hydroxide solution against phenolphthalein. The educt mixture was heated by means of an oil bath to 85°C and after reaching the temperature, it was exposed to 1.26 g catalyst (relative to the dry substance). With the addition of the catalyst a stopwatch, which was used to determine the reaction time, was started. Every 30 minutes roughly 0.5 to 1 g of sample at a time was withdrawn using a pipette. The small amounts of catalyst entrained in the sampling did not significantly influence the progression of the reaction and titrimetric acid measurement. Table III shows the measured conversions after 30 and 60 minutes reaction time.

Table III

Esterification of Ethanol and Acetic Acid

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	Conversion after 30 min (%)	Conversion after 60 min (%)
Example 1	10	13%
Example 2	20	28
Example 4	27	34

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Dehydration of Cyclohexanol

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tube reactor was heated by a temperature-controlled oil bath to 175°C, this temperature being kept constant during the experiment. To prevent gas bubble formation at this temperature, a back pressure regulator which regulated the working pressure in the reactor constantly to 30 bar was installed between the reactor and the likewise installed sampling valves. A LHSV (liquid hourly space velocity) value of 12h⁻¹ was set via the HPLC pump.

The industrial xylene used has a bromine index of 580 mg/100 g due to the unsaturated aliphatic compounds. These unsaturated compounds were reacted on the granulated catalyst presumably by a Lewis acid-catalyzed alkylation reaction such that after treatment of the raw material the bromine index dropped to values less than 2 mg/100 g. Over time, deactivation of the catalyst which allowed the bromine index of the treated xylene to rise again took place. After reaching a bromine index of 20 mg/100 g, exhaustion of the catalyst was defined. The amount of xylene converted during this running time is a direct measure of the catalyst activity. Using the granulated catalyst as shown in Example 5, a running time of 18 days was achieved, a total of 25.86 l xylene having been converted. In a comparison test with a commercially available catalyst, the Süd-Chemie product Tonsil® CO 630 G, a total running time of 12 days with a xylene throughput of 17.24 liters was achieved during this time.

The example confirms the clear improvement of catalyst activity compared to the prior art.

Claims

1. A process for producing catalysts comprising activating phyllosilicates by use of acid in the presence of catalytically active ions, wherein the catalytically active ions comprise aluminum ions, wherein a solution which is formed during acid activation is separated from a remaining solution which contains excess catalytically active cations.

2. A process for producing catalysts comprising activating phyllosilicates by use of acid in the presence of catalytically active ions, wherein the catalytically active ions comprise cerium ions, wherein a solution which is formed during acid activation is separated from a remaining solution which contains excess catalytically active cations.

3. A process for producing catalysts comprising activating phyllosilicates by use of acid in the presence of catalytically active ions, wherein the catalytically active ions comprise cerium and aluminum ions, wherein a solution which is formed during acid activation is separated from a remaining solution which contains excess catalytically active cations.

4. A process for producing catalysts comprising activating phyllosilicates by use of acid in the presence of catalytically active ions, wherein the catalytically active ions comprise iron ions, wherein a solution which is formed during acid activation is separated from a remaining solution which contains excess catalytically active cations.

5. The process of Claim 1 wherein the phyllosilicates are selected from the group consisting of smectites, chlorites, illites, vermiculites of the serpentine-kaolin group and of the sepiolite-palygorskite group including montmorillonite,

6. The process of Claim 2 wherein the phyllosilicates are selected from the group consisting of smectites, chlorites, illites, vermiculites of the serpentine-kaolin group and of the sepiolite-palygorskite group including montmorillonite, beidellite and nontronite.

8. The process of Claim 4 wherein the phyllosilicates are selected from the group consisting of smectites, chlorites, illites, vermiculites of the serpentine-kaolin group and of the sepiolite-palygorskite group including montmorillonite, beidellite and nontronite.

10. The process of Claim 3 wherein the acid activation is carried out in the presence of an earlier acid activation solution, which solution contains aluminum ions.

12. The process of Claim 4 wherein the acid activation is carried out in the presence of an earlier acid activation solution, which solution contains aluminum and iron ions.

cations are washed, dried and calcined.

14. The process of Claim 2 wherein the phyllosilicates after acid activation in the presence of catalytically active cations are washed, dried and calcined.

5 15. The process of Claim 3 wherein the phyllosilicates after acid activation in the presence of catalytically active cations are washed, dried and calcined.

10 16. The process of Claim 4 wherein the phyllosilicates after acid activation in the presence of catalytically active cations are washed, dried and calcined.

15 17. A proton-catalyzed or Lewis acid-catalyzed reaction conducted in the presence of a catalyst comprising preparing a catalyst by the process of Claim 1 and conducting the proton catalysis or Lewis acid-catalyzed reaction utilizing that catalyst.

20 18. A proton-catalyzed or Lewis acid-catalyzed reaction conducted in the presence of a catalyst comprising preparing a catalyst by the process of Claim 2 and conducting the proton catalysis or Lewis acid-catalyzed reaction utilizing that catalyst.

25 19. A proton-catalyzed or Lewis acid-catalyzed reaction conducted in the presence of a catalyst comprising preparing a catalyst by the process of Claim 3 and conducting the proton catalysis or Lewis acid-catalyzed reaction utilizing that catalyst.

30 20. A proton-catalyzed or Lewis acid-catalyzed reaction conducted in the presence of a catalyst comprising preparing a catalyst by the process of Claim 4 and conducting the proton catalysis or Lewis acid-catalyzed reaction utilizing that catalyst.

21. A process for conversion of higher olefins comprising preparing a catalyst by the process of Claim 1 and converting higher olefins with an aromatic hydroxy compound and an amine utilizing the catalyst prepared by the process of Claim 1.

5 22. A process for conversion of higher olefins comprising preparing a catalyst by the process of Claim 2 and converting higher olefins with an aromatic hydroxy compound and an amine utilizing the catalyst prepared by the process of Claim 2.

10 23. A process for conversion of higher olefins comprising preparing a catalyst by the process of Claim 3 and converting higher olefins with an aromatic hydroxy compound and an amine utilizing the catalyst prepared by the process of Claim 3.

15 24. A process for conversion of higher olefins comprising preparing a catalyst by the process of Claim 3 and converting higher olefins with an aromatic hydroxy compound and an amine utilizing the catalyst prepared by the process of Claim 4.

20 25. A catalyst for esterification, dehydration or purification of aromatics comprising preparing a catalyst by the process of Claim 1 and conducting a chemical reaction selected from the group consisting of esterification, dehydration or purification of aromatic utilizing the catalyst of Claim 1.

25 26. A catalyst for esterification, dehydration or purification of aromatics comprising preparing a catalyst by the process of Claim 2 and conducting a chemical reaction selected from the group consisting of esterification, dehydration or purification of aromatic utilizing the catalyst of Claim 2.

30 27. A catalyst for esterification, dehydration or purification of aromatics comprising preparing a catalyst by

28. A catalyst for esterification, dehydration or purification of aromatics comprising preparing a catalyst by the process of Claim 3 and conducting a chemical reaction selected from the group consisting of esterification, dehydration or purification of aromatic utilizing the catalyst of Claim 4.

Abstract

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TRANSLATION FROM GERMAN

Patent Application

Process for producing catalysts by acid activation

Specification

The invention relates a process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions.

Catalysts based on phyllosilicates, for example, clays, are used in many technical reactions. But naturally occurring clays, such as for example montmorillonite, kaolin, or attapulgite, in part have overly low activities. For this reason the clays for producing catalysts are often activated by treatment with acid. On the one hand, pure coating with for example sulfuric acid and, on the other hand, activation by extraction of the raw clay with acid, generally sulfuric or hydrochloric acid, can be done.

Thus, according to US-A-3,452,056 an acid-coated montmorillonite catalyst (KSF/0) is used for alkylation of diphenylamine. According US-A-5,672,752 an acid-extracted montmorillonite is used for the same reaction. Catalysts of this type are available under the commercial name Retrol[?], Fulcat[?] and

K10. According to US-A-5,043,511, as a replacement for corrosive homogeneous catalysts, for example AlCl_3 or BCl_3 , heterogeneous catalysts are used which are produced by coextrusion of clays with two different metal salts and thermal treatment at temperatures from 300°C to 800°C . Products produced in this way are used as catalysts for alkylation of for example benzene with olefins.

But these modified clays also have disadvantages, for example, rapid deactivation or a complex production process, and there have been many efforts to eliminate these defects. Thus, US-A-2,464,127 reports on a two-stage process with the object of obtaining amounts of iron as small as possible in the end product of acid activation of montmorillonite. According US-A-2,574,895, some of salts extracted in acid treatment are precipitated again on the montmorillonite-containing material, reducing reagents which are intended to prevent the iron from settling in the precipitation process however being used. The effort to increase the service life of the resulting catalysts by reduced coke formation is common to both applications.

DE-A-1 271 682 describes a process for activation of montmorillonite by acid extraction in the presence of inert organic liquid compounds. Strong acids, such as for example hydrochloric or sulfuric acid, are used for acid activation. Due to the presence of organic components during decomposition of the clay by acid, the lattice distances of the resulting montmorillonite catalyst are increased, by which more catalyst centers become accessible to the substrate. The catalysts according DE-A-1 271 682 are used for alkylation of phenolic compounds.

Other methods of activation are described in EP-A-352 878. In this case an untreated clay is coated by impregnation with for example zinc salts, copper salts or nickel salts. Organic solvents of the metal salts are used; the solvent is removed by distillation after impregnation. According to EP-A-144 219 and EP-A-031 252 raw clays are activated by a similar impregnation technique or by ion exchange. In ion exchange the natural intercalate cations of the minerals, mainly sodium, calcium and magnesium, are replaced by catalytically active metals. But the disadvantage in this process is that the catalysts produced in this way have an overly low pore volume. This means that only the outer surface is accessible to the substrates. Most of the inner surfaces of the catalysts are however not accessible, by which a large part of the possible activity remains unused.

To overcome this disadvantage, Laszlo in Helvetica Chimica Acta 70 (1987) 577 describes subsequent metal ion activation of already acid-activated montmorillonites. Thus, the commercially available catalyst K10 which is rich in pores and which is produced by acid activation of bentonite is modified by ion exchange with various metal salts. To do this the K10 present as a powder in a methanolic slurry is treated with solutions of the metal salts for several hours. The amount of metal ions used is computed such that they are present in a roughly 30- to 40-fold excess relative to the ion exchange capacity of the K10. Then the mixture is separated by filtration and the catalyst is washed free of salt and then dried. Especially good effects are achieved by ion exchange with aluminum salts and titanium salts; replacement with iron salts leads to improved reactivity of the catalyst only in a few cases.

A similar process is also used by Cativiela in Appl. Cat. A 123 (1995) 273. Cativiela calcinates the catalysts additionally at temperatures around 500°C in order to reduce the Brönsted activity. In this publication good activities are achieved especially with cerium salts. Replacement with iron ions however does not show any special effects.

The process used in these activation methods has at least two disadvantages. On the one hand, the process consists of two component processes which are independent of one another, specifically the acid activation of raw clays and the subsequent ion exchange reaction. Secondly, the ion exchange reaction must be carried out at a high ion excess; this necessarily leads to highly burdened waste water flows. In addition, the amounts of wash water necessary to clean the initial product after acid activation and for washing after ion exchange are very large, so that large amounts of waste water are formed thereby.

EP-B 284 397 describes a process in which the clay to be activated by the ion exchange is replaced in an upstream step with lithium ions and then thermally treated. With the resulting intermediate product ion exchange is then carried out in a second process step. Metal ions which are preferably used for this purpose are aluminum ions; Li clays with replaced iron ions do not show any improved activity compared to the initial material.

The object of this invention was to produce catalysts which have been modified with metal ions, and simple process steps and small waste water flows were to be guaranteed.

The subject matter of the invention is thus a process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions; it is characterized in that the acid activation is carried out in the presence of catalytically active metal ions and the solution which is formed during acid activation together with the residual solution which contains the excess, catalytically active cations is separated.

Preferred embodiments of the process as claimed in the invention are given in the dependent claims.

It has been surprisingly found that highly active catalysts can be obtained in the acid activation of phyllosilicates in the presence of activating ions. In doing so it is not necessary to carry out activation and ion exchange in separate process steps. In the process as claimed in the invention, completely unexpectedly small amounts of the catalytically active ions are sufficient; this can reduce process costs, but also the environmental burden of the process to a minimum. In certain cases, as for example in activation with iron ions or aluminum ions, the spent liquors obtained in this way can even be used as precipitation aids in the clean-up of municipal sewage. It has furthermore been ascertained that the metal ions used for modification are present in an especially high degree of activation so that the amount of metal ions present in the final product can be kept especially low.

The subject matter of the invention is also the use of catalysts which can be obtained using the process as claimed in

the invention for proton-catalyzed reactions, especially for conversion of higher olefins with aromatic hydroxy compounds and amines, for esterification and dehydration reactions as well as for purification of xylene and for Lewis acid-catalyzed reactions, such as for example alkylation of aromatics.

The invention is explained by the following examples.

Example 1

Comparison catalyst

A previously dried Bavarian montmorillonite-containing raw clay with an ion exchange capacity (IUF) of 80 mVal/100 g was decomposed by hydrochloric acid treatment.

To determine the acid exchange capacity (IUF), the phyllosilicate to be studied is dried over an time interval of 2 hours at 150°C. Then the dried material is reacted with an excess of aqueous 2N NH_4Cl solution for one hour with reflux. After a holding time of 16 hours at room temperature it is filtered, whereupon the filter cake is washed, dried and ground and the NH_4 content in the phyllosilicate is determined by nitrogen determination (CHN analyzer from Leo). The proportion and type of exchanged metal ions are determined in the filtrate by ICP spectroscopy.

During decomposition, 90.3 g of raw clay with a water content of 16.9% by weight together with 250.7 g water and 87.5 mg of 30% hydrochloric acid were treated in a three-neck flask

with a reflux condenser for 8 hours at the boiling point. Afterwards the mother liquor was separated from the product by filtration by means of a Buchner funnel and washed using demineralized water until chloride could no longer be detected in the wash water. The washed filter cake was dried at a temperature of 120°C and then ground.

The product obtained in this way has a BET surface of 253 m²/g (according to DIN 66131) and a pore volume of 0.403 ml/g (determined by nitrogen adsorption and evaluation of the adsorption isotherms using the BJH method - E.P. Barret et al., J.Am.Chem.Soc. 73 (1951) 373). The pore distribution curve obtained from BJH derivation showed a Gaussian distribution with a maximum at 5.5 nm. The material contained among others the following exchangeable metal ions:

Fe ³⁺	1.0 mVal/100 g
Al ³⁺	11.4 mVal/100 g
Ce ³⁺	< 0.1 mVal/100 g

Example 2

Iron-containing catalyst

A Bavarian montmorillonite-containing raw clay with an ion exchange capacity IUF of 92 mVal/100 g was activated analogously to example 1. In addition to the reagents indicated in Example 1, iron chloride in the form of a concentrated FeCl₃ solution was added to the batch. The following were used for this batch:

Raw clay (17.2 % by weight H ₂ O)	82.8 g
Water	250.3 g
HCl (30%)	50.0 g
FeCl ₃ solution (2.5 mole Fe/kg)	6.0 g

The product obtained in this way had a BET surface of 290 m²/g and a pore volume of 0.338 ml/g. The peak of the pore distribution curve was at 4.6 nm. The amount of exchangeable Fe³⁺ ions was 2.0 mVal/100 g.

Example 3

Iron-containing catalyst

Example 2 was repeated using 18.0 g FeCl₃ solution:

The product obtained in this way had a BET surface of 400 m²/g and a BJH pore volume of 0.491 ml/g. The peak of the pore distribution curve was at 4.7 nm. The amount of exchangeable Fe³⁺ ions was 8.0 mVal/100 g.

Example 4

Aluminum-containing catalyst

Example 2 was repeated using 7.24 g AlCl₃ * 6 H₂O.

The product obtained in this way had a BET surface of 315 m²/g and a BJH pore volume of 0.425 ml/g. The peak of the pore distribution curve was at 3.3 nm. The product contained 18.0

mVal/100 g exchangeable Al^{3+} .

Example 5

Cerium-containing catalyst

A montmorillonite-containing raw clay from Turkey was dried to a water content of roughly 15% by weight and was ground. The material with a resulting water content of 13.1% by weight was activated as described in Example 1, the reaction mixture having been enriched with $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$. The following were used for this batch:

Raw clay (13.1 % by weight H_2O)	86.3 g
Water	254.6 g
HCl (30% by weight)	62.5 g
$\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$	13.03 g

Analysis of the product yielded a BET surface of $379 \text{ m}^2/\text{g}$ and a BJH pore volume of 0.431 ml/g . The peak of the pore distribution curve was at 3.0 nm , the product contained 5.1 mVal/100 g exchangeable Ce^{3+} .

Example 6

Reaction of phenol with nonene

The alkylation example 11 of DE-A-1 271 682 was reworked analogously. In a 1 liter three-neck flask equipped with a thermometer, a magnetic stirring mechanism and a reflux

condenser, 252.5 g (2.0 mole) nonene, 235.3 g (2.5 mole) phenol and 5.0 g catalyst from Example 2 and Example 3 were heated to 90°C. After 3 hours reaction time, the catalyst was filtered off. The filtrate was fractionated using a 10 cm Vigreux column. In the boiling range from 159°C to 181°C the alkylation product nonyl phenol was obtained.

As Table I shows, higher yields are achieved with the catalysts as claimed in the invention compared to the undoped catalyst (Example 1). The narrower boiling range for Fe-modified catalysts indicates a more uniform product spectrum and thus higher selectivity of the Fe-containing catalysts.

Table I

Alkylation of Phenol with Nonene

Catalyst	Boiling range of product	Yield
Example 1	160 - 180°C	35.3%
Example 2	165 - 175°C	38.7%
Example 3	173 - 175°C	41.2%

Example 7

Reaction of diphenylamine with nonene

In a 500 ml three-neck flask, 42.5 g (0.25 mole) diphenylamine were heated to roughly 150°C and melted. Then 5.0 g catalyst and 44.2 g (0.35 mole) nonene were added to the melt. After a reaction time of 4 h, a further 41.6 g (0.33 mole) nonene

were added, the reaction temperature of 150°C having been maintained. After a reaction time of 8 h the reaction mixture was separated from the catalyst by filtration. The yield of dialkylated diphenylamine was determined by infrared spectroscopy using the following formula:

$$(\%) \text{ dialkylate} = [\text{Log}(\text{ext@ } 820 \text{ cm}^{-1} / \text{ext@ } 743 \text{ cm}^{-1}) + 1.141] / 0.019;$$

ext@ extinction (absorbance) at the indicated wave number. In doing so it was considered that the adsorption peak at 820 cm^{-1} corresponds to the dialkylated products, the adsorption peak at 743 cm^{-1} corresponds to the monoalkylated products. The reaction mixture was measured at a layer thickness of 0.025 mm to determine extinction.

Table II lists the determined yields of the reaction with various catalysts.

Table II

Alkylation of Diphenylamine with Nonene

Catalyst	Yield of dinonyl-diphenylamine (%)
Example 1	27
Example 2	40
Example 3	37
Example 4	35

The example confirms the improved activity of the catalysts as claimed in the invention in diphenylamine alkylation compared

Esterification of acetic acid and ethanol

In a 250 ml three-neck flask with a thermometer, a magnetic stirring mechanism and a reflux condenser, 72.0 g acetic acid and 55.2 g ethanol were mixed. Roughly 0.5 g was removed from the mixture, and the acid content was determined by titration with 0.1N sodium hydroxide solution against phenolphthalein. The educt mixture was heated by means of an oil bath to 85°C and after reaching the temperature, it was exposed to 1.26 g catalyst (relative to the dry substance). With the addition of the catalyst a stopwatch which was used to determine the reaction time was started. Every 30 minutes roughly 0.5 to 1 g of sample at a time was withdrawn using a pipette. The small amounts of catalyst entrained in the sampling do not significantly influence the progression of the reaction and titrimetric acid measurement. Table III shows the measured conversions after 30 and 60 minutes reaction time.

The example confirms the constantly high reactivity of the catalysts for proton-catalyzed reactions.

Example 10

Continuous Purification of Xylene

Some of the filter cake obtained after washing the product according to Example 5 was dried at 110°C and carefully crushed. The 0.25 mm to 0.50 mm grain fraction was screened out of the fragments. Five milliliters of these fractional granulates was placed in a 10 ml tube reactor through which industrial xylene flowed continuously via a HPLC pump. The tube reactor was heated by a temperature-controlled oil bath to 175°C, this temperature being kept constant during the experiment. To prevent gas bubble formation at this temperature, a back pressure regulator which regulated the working pressure in the reactor constantly to 30 bar was installed between the reactor and the likewise installed sampling valves. A LHSV (liquid hourly space velocity) value of 12h^{-1} was set via the HPLC pump.

The industrial xylene used has a bromine index of 580 mg/100 g due to the unsaturated aliphatic compounds. These unsaturated compounds were reacted on the granulated catalyst presumably by a Lewis acid-catalyzed alkylation reaction such that after treatment of the raw material the bromine index dropped to values less than 2 mg/100 g. Over time, deactivation of the catalyst which allowed the bromine index of the treated xylene to rise again took place. After reaching a bromine index of 20 mg/100 g, exhaustion of the catalyst was defined. The amount of xylene

converted during this running time is a direct measure of the catalyst activity. Using the granulated catalyst as shown in Example 5, a running time of 18 days was achieved, a total of 25.86 l xylene having been converted. In a comparison test with a commercially available catalyst, the Süd-Chemie product Tonsil⁷ CO 630 G, a total running time of 12 days with a xylene throughput of 17.24 liters was achieved during this time.

The example confirms the clear improvement of catalyst activity compared to the prior art.

Claims

1. Process for producing catalysts by acid activation of phyllosilicates and modification with catalytically active metal ions, characterized in that acid activation is carried out in the presence of catalytically active metal ions and the solution which forms during acid activation together with the remaining solution which contains the excess, catalytically active cations is separated.

2. Process as claimed in claim 1, wherein acid activation is carried out in the presence of iron ions, aluminum ions, and/or cerium ions.

3. Process as claimed in claim 1 or 2, wherein phyllosilicates from the group of smectites, chlorites, illites, vermiculites of the serpentine-kaolin group, and of the sepiolite-palygorskite group, especially montmorillonite, beidellite and nontronite, are used.

4. Process as claimed in one of claims 1 to 3, wherein acid activation is carried out in the presence of a waste liquor from earlier acid activation, which liquor contains aluminum ions and/or iron ions.

5. Process as claimed in one of claims 1 to 4, wherein the acid-activated phyllosilicates which are coated with the catalytically active metal ions are washed, dried and calcinated.

6. Use of catalysts which can be obtained using the process as

Abstract

A process for producing catalysts by acid activation of phyllosilicates and coating with catalytically active metal ions is described. Acid activation is carried out in the presence of catalytically active metal ions and the solution which forms during acid activation together with the remaining solution which contains the excess, catalytically active cations is separated. The catalysts can be used for proton-catalyzed and Lewis acid-catalyzed reactions, especially for conversion of higher olefins with aromatic hydroxy compounds and amines, for esterification and dehydration reactions and for purification of aromatics.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Includes Reference to PCT International Applications)

P-1118

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR PRODUCING A CATALYST BY ACID ACTIVATION

the specification of which (check only one item below):

☐ is attached hereto.☒ was filed as United States application

Serial No 10/049,744

on January 30, 2002

and was amended

on (if applicable).

☐ was filed as PCT international application

Number

on

and was amended under PCT Article 19

on (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (If PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day month year)	PRIORITY CLAIMED UNDER 35 USC 119
PCT	PCT/EP 00/06507	09 July 2000	<input type="checkbox"/> YES <input type="checkbox"/> NO
Germany	199 35 914.8	30 July 1994	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
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Combined Declaration For Patent Application and Power of Attorney (Continued)				ATTORNEY'S DOCKET NUMBER P-1118	
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U.S. APPLICATIONS			STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
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PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			
PCT/EP 00/06507	09 July 2000				
<p>POWER OF ATTORNEY As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number)</p> <p style="text-align: center;">Scott R. Cox Reg. No. 31,945</p>					
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